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<p><b>(21) International Application Number:</b> PCT/GB99/02773</p> <p><b>(22) International Filing Date:</b> 6 September 1999 (06.09.99)</p> <p><b>(30) Priority Data:</b>          9819397.2      7 September 1998 (07.09.98)      GB</p> <p><b>(71) Applicant (for all designated States except US):</b> MACGRE-          GOR, Keith, Martin [GB/GB]; P.O. Box 2, Ilkley, West          Yorkshire LS29 9YB (GB).</p> <p><b>(72) Inventor; and</b></p> <p><b>(75) Inventor/Applicant (for US only):</b> GIBBS, Anthony, Marston          [GB/GB]; 19 Grange Close, Ludham, Great Yarmouth,          Norfolk NR29 5PZ (GB).</p> <p><b>(74) Agent:</b> APPELYARD LEES; 15 Clare Road, Halifax HX1 2HY          (GB).</p>		<p><b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG,          BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB,          GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG,          KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK,          MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI,          SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA,          ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ,          UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD,          RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK,          ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI          patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR,          NE, SN, TD, TG).</p> <p><b>Published</b>  <i>With international search report.          Before the expiration of the time limit for amending the          claims and to be republished in the event of the receipt of          amendments.</i></p>
<p><b>(54) Title:</b> COMPOSITION FOR THE REMOVAL OF BIOLOGICAL AND ORGANIC SUBSTANCES</p> <p><b>(57) Abstract</b></p> <p>The present invention relates to a composition for and an improved method of removing all types of biologically-generated soiling. The invention is concerned with the removal of the biological source of the soiling without resorting to the type of chemical activity generally associated with disinfection. In particular the invention concerns the removal from surfaces of algae and similar organisms, including many organisms which secrete substances for purpose of securing the organism to a surface.</p>		

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**Composition for the removal of biological and organic  
substances**

5 The present invention relates to a composition for and an improved method of removing all types of biologically-generated soiling. The invention is also concerned with the actual removal of the biological source of the soiling without resorting to the type of chemical activity generally associated with disinfection.

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The present invention relates in particular to the removal from surfaces of algae and similar organisms, including many organisms which secrete substances for purpose of securing the organism to a surface.

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The compositions of the present invention serve to modify these biological secretions. Biological substances which are secreted by certain organisms, together with organic and other inorganic substances, form the basis of the adhesion of an organism whether it be micro, macro or larger to surfaces. This adhesion makes it difficult for traditional methods of removal of the organism from the surface to be totally effective. As a result, the quality of hygiene treatments or other subsequent treatments following to the removal of surface contamination from biological sources is reduced greatly.

Common methods of removing biologically generated soils generally require the use of a suitable surface active agent. Additives are generally included in known preparations for the purpose of improving the soil-

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lifting properties of the surface active agent.

Other known preparations have conventionally employed cell toxins which are commonly described as disinfectant agents. These substances have very little or no actual activity in releasing such organisms from a surface. Hence, although the cells are destroyed many will remain on a contaminated surface thereby providing nutrients for further colonisation by a subsequent contaminant.

10 However, a number of problems arise when using traditional compositions, and although these may be minimised by devising suitable formulations, the result is often a compromise in terms of the cleaning properties, safety or ease of use. Conventional agents may be highly toxic and/or corrosive thereby presenting a hazard to the user and requiring the use of specialist protective clothing. Certain treatments may be subject to statutory limitations to their use or be only suitable for professional application. Containment of the cleaning agent only to the desired area may therefore also be an issue. This is particularly relevant where biological or other complex organic contamination is present and aggressive or corrosive agents have traditionally been required.

30 Whilst the toxin or other cell inhibitor present in conventional preparations may well have a wide spectrum of activity and thus be effective, there is the problem that areas adjacent to that being treated may need to be protected or other safety precautions may be necessary to

prevent the spread of the toxic and/or corrosive agent. This represents both an increased risk and cost when using such agents.

5 In addition, there are certain areas in which highly aggressive cleaning agents simply would not be compatible with the environment in which they are required, for example the use of most toxin-containing cleaning formulations would be a health hazard in algae removal  
10 from around swimming pools, paths and patios, occupied buildings or the like. These areas are all touched or subject to human or animal contact.

The present invention seeks to provide an effective  
15 cleaning composition which is not aggressive or corrosive and does not pose a hazard to the user or to the external environment. The composition is also intended to be economical to manufacture and easy to use without any special training or equipment. It is also an aim to  
20 provide a treatment which ideally is able to prevent the re-occurrence of contamination at a treated site.

The present invention achieves these various aims and overcomes the difficulties inherent in the prior art  
25 using formulations which address the way in which the unwanted contamination such as an organism is secured to a surface.

According to the present invention, there is provided a  
30 composition comprising:

- (i) an alkyl or aryl amine, or an amine donor selected from: a Group III metal-amino chelate, lauryl dimethyl benzyl ammonium chloride (BAC) or cetyl trimethyl ammonium bromide;
- 5 (ii) a complexing agent selected from: an oxazole, a thiazole, an isoxazole, an isothiazole; and biguanide polymer;
- (iii) a Group III B element selected from Al, Ga or In the form of a salt or complex ion;
- 10 (iv) a carrier; and optionally
- (v) a d-block element in the form of a salt or complex ion; and
- (vi) a viscosity modifier and/or a catalyst.

Immobile organisms rely on surface adhesion for security  
15 and life support and thus multiplication. The composition of the present invention is effective against surface contamination by both breaking the bond between the contaminant and the surface, and by directly attacking the contaminant itself, thereby preventing its  
20 continual propagation.

The invention provides a broad spectrum micro-organism and macro-organism cell release mechanism. In cases, and with specific reference to algal and similar cells, removal will provide sufficient treatment to ensure the  
25 biological safety of a surface with regard to contamination or health. In many cases, the compositions of the present invention also serve to inhibit cell

development in addition to ensuring their removal from the surface.

Where a further degree safety i.e sterility of the surface is required, the release of microbic cells from a surface using the compositions of the present invention allows traditional disinfection or sterilisation treatment to be more effective. The reason is that any organic matter which would normally reduce the anti-microbic activity of a disinfectant will no longer be present in the case of surface treatment with compositions according to the present invention.

A composition comprises the above complexing agents and may include auxiliary complexing agents. Such auxiliary complex agents may be salts of transition elements, for example of copper with an organic acid such as lactic, citric or ascorbic acids.

Algal cell-release compositions of the invention may thus comprise a complexing agent(s) selected from one or more salts of an organic acid and a transition metal, a salt of a group III metal or a d-block metal salt, a carrier capable of assisting wetting preferably a non-ionic or amphoteric surfactant, and a cationic moiety wherein the moiety is part of a chemically-independent compound or chemically associated with the carrier or complexing agent.

Preferably, the amine donor is lauryl dimethyl benzyl ammonium chloride, benzalkonium chloride or cetyl trimethyl ammonium bromide. The amine donor may be in the form of a free base or a salt. When an amine is

provided as component (i), whether in place of or in addition to the amine donor, the amine is preferably a lower alkyl amine having one or more alkyl substituents each being C<sub>6</sub> or less, or a single aryl substituent and 0, 1 or 2 alkyl substituents of C<sub>6</sub> or less. The amine may be in the form of a free base or a salt.

The complexing agent is preferably 1, 2 benzisothiazolin-3-one, 2-methyl-4, 5-trimethylene-4-isothiazolin-3-one, or polymeric biguanide hydrochloride.

The Group III B element may be in the form of a salt or in the form of a metal amino chelate of that salt. The Group III B element is preferably aluminium. Aluminium chloride or aluminum amino chelates, such as aluminium amino sulphate, are particularly preferred. If the Group III B element is metal amino chelate then components (i) and (iii) of the composition may be identical, or they may be different components of the composition.

The component containing the d-block element is not essential to the effective working of the formulations of the present invention. However, by including both a Group III B element and a d-block element a substantial improvement in efficacy may be noted. In particular, the component containing the d-block element improves the activity against soils secreted by algae and the like.

Preferred d-block elements, when present, include iron, copper, manganese and zinc. Copper is particularly preferred.

Preferably, the salts of the Group III B element or the d-block element contain halo, sulphate, nitrate, citrate,



tartrate, or oxalate anions. However, any salt which is stable and soluble in water will suffice.

The carrier is inert with respect to reaction with the other components of the formulation and may be water or a suitable organic solvent such as methanol, ethanol, ethylene glycol or isopropanol or a mixture containing some or all of the above-mentioned solvents. Isopropanol in combination with water is particularly preferred. The carrier may also be a conventional cationic or non-ionic surfactant, or an aromatic ester in aqueous solution.

Typical carriers for solid and powder formulations include simple solid alkali carbonates and polyphosphates, or cross-linked polyacrylates or other inert material such as pumice dust or wood flour. The carrier may also be in the form of a complex silicate salt (formulations containing complex silicates can be used to treat new concrete or other materials of construction thereby rendering such surfaces algae repellent).

In an embodiment of the invention, the composition may be absorbed into a porous matrix of carrier material to increase surface area of the composition or to control the release of the composition.

Alternatively, salts of at least one component of the composition may have a reduced solubility in the carrier so that the rate of release can be controlled as required.

The composition in accordance with the present invention may be provided in a liquid, gel, solid or powder form.

As an optional feature, the compositions of the present invention, when in liquid or gel form, may also include a conventional viscosity modifier such as cellulose or xanthan gum in order to make the composition easier to handle and use.

As an optional feature, the compositions of the present invention may also include a catalyst.

Preferably, the catalyst is an immobilised biological catalyst which functions to further reduce the cell adhesion to a surface.

The composition of the present invention preferably comprises based on 100% activity, by weight:

2 to 50%, and more preferably 5 to 8% inclusive, of the alkyl or aryl amine, or the amine donor;

0.1 to 10%, and more preferably 0.5 to 1.0% inclusive, of the complexing agent;

0.05 to 4%, and more preferably 0.05 to 0.50%, inclusive of the salt or complex ion of the Group III B element;

0.05 to 4%, and more preferably 0.05 to 0.50%, inclusive, of the d-block element when present; and

up to 10%, inclusive, of additives when present;

with the balance of the composition comprising the carrier.

5

Within the scope of the above mentioned ranges, the proportions may be varied to suit particular conditions or requirements.

- 10 The compositions of the present invention, whether in liquid, gel, solid or powder form, provide a concentrate for dilution prior to application. From 10 to 100 mls of a liquid or gel formulation is diluted in 1000 mls of water for application to a surface. In the case of solid  
15 or powder formulations, from 5 to 50 gms of the composition is dissolved in 1000 mls of water for application to a surface.

- The precise mechanism whereby the compositions of the  
20 present invention operate is not presently understood. However, it is thought that the composition reduces the adhesion between microbic cells and the surface.

- In particular, it is believed that the compositions  
25 target secretions from macro-organisms such as algal cells. This reduces the ability of the cells to absorb nutrients and thus the cells weaken and can be removed easily by mechanical means and can be more effectively destroyed by traditional methods such as disinfectants.

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In some cases, the compositions may exert a direct

cytotoxic effect on the organisms in situ in addition to performing the function of removing the organism from the surface. On some surfaces there also appears to be a residual effect after treatment which further reduces the development or re-contamination of a treated surface. This is a significant advantage of the compositions of the present invention since frequent treatment is therefore not necessary. The compositions of the present invention also have the benefit of reducing noxious odours associated with certain secretions from microorganisms. The treatment can thus provide effective odour control in many cases.

The following compositions which are effective against algal contamination and the like are presented by way of example only.

#### Example 1

An aqueous formulation for subsequent dilution prior to application to a surface was prepared from the following components, expressed as % by weight:

	lauryl dimethyl benzyl ammonium chloride	4.1%
25	2-methyl-4, 5-trimethylene-4-isothiazolin-3-one	0.37%
	aluminium ammonium sulphate	2.4%
	copper citrate	3.5%
	non-ionic surfactant	0.5%
	isopropyl alcohol	5.0%
30	deionised water	to 100%

## Example 2

An aqueous formulation for subsequent dilution prior to application to a surface was prepared from the following components, expressed as % by weight:

	benzalkonium chloride	6%
	aluminium chloride	0.06%
	polymeric biguanide hydrochloride	0.60%
10	sodium benzoate	0.05%
	isopropyl alcohol	3.0%
	deionised water	to 100%

The concentrated aqueous formulations were diluted with water, in the ratio of 50 mls of concentrate per 1000 mls of water, and applied to an external paved area test site on which extensive algal contamination had been cultivated. The adhered algae was easily lifted by rinsing with water or brushing following the application of the diluted formulation to the whole area. No recontamination with algae had appeared six months after treatment.

## CLAIMS

1. A composition comprising:
  - 5 (i) an alkyl or aryl amine, or an amine donor selected from: a Group III metal-amino chelate, lauryl dimethyl benzyl ammonium chloride (BAC) or cetyl trimethyl ammonium bromide;
  - (ii) a complexing agent selected from: an oxazole, a  
10 thiazole, an isoxazole, an isothiazole; and biguanide polymer;
  - (iii) a Group III B element selected from Al, Ga or In the form of a salt or complex ion;
  - (iv) a carrier; and optionally
  - 15 (v) a d-block element in the form of a salt or complex ion; and
  - (vi) a viscosity modifier and/or a catalyst.
2. A composition as claimed in claim 1 further  
20 comprising a salt of a transition element with an organic acid as an auxiliary complexing agent.
3. A composition as claimed in claim 1 or 2, wherein the amine donor is lauryl dimethyl benzyl ammonium chloride, benzalkonium chloride or cetyl trimethyl ammonium bromide.
- 25 4. A composition as claimed in claim 1 or 2, wherein an amine is provided as component (i) in place of or in

addition to the amine donor and the amine is a lower alkyl amine having one or more alkyl substituents each being C<sub>6</sub> or less, or a single aryl substituent and 0, 1 or 2 alkyl substituents of C<sub>6</sub> or less.

- 5 5. A composition as claimed in any preceding claim, wherein the complexing agent is 1, 2 benzisothiazolin-3-one, 2-methyl-4, 5-trimethylene-4-isothiazolin-3-one, or polymeric biguanide hydrochloride.
- 10 6. A composition as claimed in any preceding claim, wherein the salt or complex ion of the Group III B element is aluminium chloride or aluminium amino sulphate.
- 15 7. A composition as claimed in any preceding claim, wherein the d-block element is selected from the group comprising: iron, copper, manganese and zinc.
8. A composition as claimed in any preceding claim which comprises by weight based on 100% activity:
- 20 2 to 50%, and more preferably 5 to 8% inclusive, of the alkyl or aryl amine, or the amine donor;
- 0.1 to 10%, and more preferably 0.5 to 1.0%, inclusive, of the complexing agent;
- 0.05 to 4%, and more preferably 0.05 to 0.50%, inclusive, of the salt or complex ion of the Group
- 25 III B element;
- 0.05 to 4%, and more preferably 0.05 to 0.50%, inclusive, of the d-block element when present; and

up to 10%, inclusive, of additives when present; with the balance of the composition comprising the carrier.

9. A liquid or gel composition as claimed in any preceding claim diluted with from 10 to 100 parts of water.
10. A solid or powder composition as claimed in any of claims 1 to 8, diluted with water so that each 1000 mls of the diluted composition contains from 5 to 50 gms of the solid or powder.
11. A method of removing algae from a surface, the method comprising the steps:
  - (a) diluting the composition of any of claims 1 to 8 with water to produce a diluted composition;
  - 15 (b) applying the diluted composition to the surface;
  - (c) optionally applying mechanical force to the surface; and
  - (d) rinsing the diluted composition and algae from the surface with water.
12. A method as claimed in claim 11, wherein one part of a liquid or gel composition is diluted with from 10 to 100 parts of water.
13. A method as claimed in claim 11, wherein a solid or powder composition is diluted so that 1000 mls of



the diluted composition contain from 5 to 50 gms of the solid or powder.

## INTERNATIONAL SEARCH REPORT

Int. Application No.  
PCT/GB 99/02773

## A. CLASSIFICATION OF SUBJECT MATTER

C11D1/62, C11D1/50, C11D3/48, A01N33/02

According to International Patent Classification (IPC) or to both national classification and IPC 7

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D, A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI, Week 198912, Derwent Publications Ltd., London, GB; Class A01N33/04, AN 1989-090795; & JP 01 042406 A (NITTO BOSEKI CO. LTD.) 14 February 1989, abstract.	1, 3
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☒ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

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-2-

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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## ANHANG

## ANNEX

## ANNEXE

zum internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

to the International Search  
Report to the International Patent  
Application No.

au rapport de recherche brevet  
international relatif à la demande de brevet  
international n°

FCT/GB 99/02773 SAE 248300

In diesem Anhang sind die Mitglieder  
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This Annex lists the patent family  
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